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This study compared gravimetric and photometric aerosol sampling instruments for determining airborne concentrations of particulate matter. The instruments used were (1) the SKC? Deployable Particulate Sampler (DPS) that collects a sample on a filter, which is gravimetrically analyzed for concentration of mass, and (2) the TSI? DustTrak? 8520 and Sidepak?AM510 that use photometry to estimate airborne particulate concentration. The capability to use these samplers interchangeably would permit employment of the best-suited instrument based on logistical and mission parameters for military force health protection. The instruments were deployed at Yuma Proving Grounds, Arizona for testing and were used in side-by-side sampling over a period of 13 days. Three statistical analyses, Pearson correlation coefficient, correlation within means, and the Bland-Altman analysis were used to compare the derived data. Statistical interpretation of the data between the DPS and the DustTrak at the PM10 cut-point found a strong correlation of data using the metric devised for this study measuring the strength of a relationship between two variables. Analytical comparisons for the DPS and DustTrak at the PM2.5 cut-point demonstrated a weak relationship. The analysis between the DPS and the SidePak was not possible as the power source did not enable the Sidepak to sample for a twentyfour hour period and thus the samples collected were not comparable. A requirement exists for further laboratory and field studies.

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Abstract

A Comparison of Gravimetric and Photometric Aerosol Samplers

by

Captain Donald W. McInnes, Master of Science in Public Health, 2009

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This study compared gravimetric and photometric aerosol sampling instruments for determining airborne concentrations of particulate matter. The instruments used were (1) the SKC® Deployable Particulate Sampler (DPS) that collects a sample on a filter, which is gravimetrically analyzed for concentration of mass, and (2) the TSI® DustTrak™ 8520 and Sidepak™AM510 that use photometry to estimate airborne particulate concentration. The capability to use these samplers interchangeably would permit employment of the best-suited instrument based on logistical and mission parameters for military force health protection. The instruments were deployed at Yuma Proving Grounds, Arizona for testing and were used in side-by-side sampling over a period of 13 days. Three statistical analyses, Pearson correlation coefficient, correlation within means, and the Bland-Altman analysis were used to compare the derived data. Statistical interpretation of the data between the DPS and the DustTrak at the PM_{10} cut-point found a strong correlation of data using the metric devised for this study measuring the strength of a relationship between two variables. Analytical

comparisons for the DPS and DustTrak at the $PM_{2.5}$ cut-point demonstrated a weak relationship. The analysis between the DPS and the SidePak was not possible as the power source did not enable the Sidepak to sample for a twenty-four hour period and thus the samples collected were not comparable. A requirement exists for further laboratory and field studies.

A Comparison of Gravimetric and Photometric Aerosol Samplers

by

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A thesis submitted to the Faculty of the Department of Preventive Medicine and Biometrics, Uniformed Services University of the Health Sciences in partial fulfillment of the requirements for the degree

of

MASTER OF SCIENCE IN PUBLIC HEALTH, 2009

Preface

The conduct of this study was in collaboration with the Canadian Forces (Force Health Protection). The specific aims of this research were: to collect ambient air sampling data and compare the SKC® Deployable Particulate sampler to the TSI® DustTrak™ and the SidePak™ at the 2.5 and 10-micrometer cut-point for particulate matter; to establish if a relationship between data exists; and evaluate the effectiveness, suitability, and performance of the systems in a desert environment

Dedication

I dedicate this Master of Science in Public Health thesis to my wife, Noreen and my daughters Molly Blain and Charlotte Emily. Thank you for all your support and sacrifices.

-Donald

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I thank Canadian Forces Directorate of Force Health Protection for supporting me in this endeavour.

I thank the United States Army Center for Health Promotion and Preventive Medicine and the United States Army Garrison-Yuma, Environmental Sciences Division for their logistical support required to complete this work. Without their assistance, this study would not have been possible.

Special thanks to CDR Philip Smith his mentoring and confidence in my abilities.

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Definition of Terms

a) Aerodynamic diameter – the diameter of a unit-density sphere having the same gravitational settling velocity (terminal velocity) as the particle being sampled (Johnson, *et* al., 2003; Spurny, 1998).

b) Aerosol - particulate matter that is a solid or liquid droplet larger than a molecule but small enough to remain suspended in the atmosphere. Natural sources include salt particles from sea spray, dust and clay particles, and volcanic matter carried by the wind. Anthropogenic aerosols can originate from automobiles, combustion industries, and nuclear incidents, intentional or not. Many human generated aerosols are considered pollutants (Vincent, 2007).

c) Cut-off particle diameter – median diameter of a range of particle sizes which will impact on a stage of a cascade impactor; also called the 50% cut-point, cut-point, d_{50}, or the effective cut-off diameter (Willeke and Baron, 1993).

d) Dusts – dry particle aerosols generated physically in nature through the process of wind erosion or geologic interactions. Some of these processes are dust storms or volcanic activity. Typical production of anthropogenic sources is from dynamic mechanical attrition in mining and construction through the processes of crushing, pulverizing, blasting, drilling, and grinding. Dusts are also produced in dry material preparations and packaging processes. Dusts can create human

exposure hazards due to their small size and high specific surface area. Dust particles range in size from 1.0 μm to 100 μm with shapes that are often aerodynamically spherical (Johnson, *et* al., 2003 and Vincent, 2007).

e) Fibers – are particles defined as having an aspect ratio of greater than 3:1. Respirable fibers are usually 5 to 10 μm in length and have a diameter of less than 3.0 μm. Natural fibers come from plants or asbestiform silicate minerals. They can also be anthropogenic in nature as in the case of vitreous or graphite fibers. Fibrous aerosol particles display aerodynamic and health effect behaviours different in some respects to those of spherical or nearly spherical particles of the same material and mass. Aerosol characterization is typically more complex for fibers than for other aerosols due to the difficulty in comparability, assessing the size, and nature of the fiber surface area. Small fibers, less than 2 μm, are considered nuisance dusts while fibers longer than 5.0 μm have the potential to cause disease (Vincent, 2007; Meldrum, 1996; and ATSDR, 2001).

f) Fog – discernible mist that floats in air and usually settles to the ground or water. Production of fog is by the condensation of water or liquid vapour into minute liquid droplets in air. Fog particles range in size from 1 to 10 μm (Hinds, 1999 and McDermott, 1985).

g) Fumes – very fine solid particle aerosols produced by the condensation of vapours or gaseous combustion products derived from solids. Materials that are solids at standard temperature and pressure, when heated to a sufficient degree will vaporize. In the case of a metal, the vapour rises

and as it cools, it forms spherical molten droplets that further condense to form spherical solid particles. The smelting of metals or welding, e.g., arc, and plasma welding, create fumes. These activities produce large volumes of vaporous material that includes fume particles and various gases. Fume particles are less than 1 μm in diameter (Johnson, *et al*., 2003 and Vincent, 2007).

h) Impact sampler – a PM impactor initially inspires the aerosol through the impactor inlet and then efficiently removes particles larger than the stated cut-point by capturing them on a disposable oiled impaction substrate that reduces particle bounce. Particles smaller than the nominal cut-point are then collected on the appropriate size and type of filter. (SKC, 2006).

i) Inches of mercury (in Hg) – a traditional unit of pressure measurement. Standard atmospheric pressure is 29.92 in Hg or 101.325 kPa. This unit is not associated with the Système International d'Unités or the centimeter-gram-second units; however, in Hg is widely used.

j) Light scattering or particle count – particles in the aerosol stream scatter light in all directions. A lens at right angle to both the aerosol stream and laser beam collects some of the scattered light and focuses it onto a photodetector. The detection circuitry converts the light into a voltage. The voltage is proportional to the amount of light scattered which is ideally proportional to the mass concentration of the aerosol (TSI, 2002).

k) Mist – a spherical liquid particle aerosol formed by condensation or atomization, such as spraying or arising from acid baths in chrome plating. The droplets are homogenous with the parent material and range from

sub-micrometers to 100 μm (Willeke and Baron, 1993; Johnson, *et* al., 2003 and Vincent, 2007).

l) Particulate matter (PM) – airborne PM includes both solid particles and liquid droplets, is emitted naturally or anthropogenically, and found in a wide range of sizes (NAAQS, 2006).

m) Particulate matter 2.5 ($PM_{2.5}$) – aerosol PM with an aerodynamic diameter less than or equal to a nominal 2.5 μm. $PM_{2.5}$ is referred to as fine PM and is postulated to pose the largest health risk because particles of this size range can migrate and deposit deep into the lungs (EPA, 2008).

n) Particulate matter 10 (PM_{10}) – aerosol PM with an aerodynamic diameter less than or equal to a nominal 10 μm but greater than 2.5 μm. PM_{10}, also known as coarse PM, poses a health concern because these particles can accumulate in the upper respiratory tract and may cause illness (EPA, 2008).

o) Performance – the manner in which the instruments operated or functioned with regard to effectiveness in sampling airborne particulate matter.

p) Smoke – is visible and results from the incomplete combustion of carbonaceous material. Smoke can consist of solids, liquids, gases, and vapours. Smoke particles are usually 0.01 to 1 μm in diameter; however, particles tend to agglomerate into larger masses. Smoke from burning material can be toxic (Hinds, 1999).

q) SKC® Deployable Particulate Sampler (DPS) System – compact, battery operated, portable particulate sampler manufactured by SKC® Inc, Eighty

Four, PA, USA. The DPS can sample PM indoors and outdoors, and in urban, rural, or industrial environments.

r) TSI® SideTrak™ 8520 - compact, battery operated, photometric, portable aerosol monitor manufactured by TSI® Inc., Shoreview, MN, USA. The DustTrak can monitor PM indoors and outdoors, and in urban, rural, and industrial environments.

s) TSI® SidePak™ AM510 - compact, battery operated, photometric, personal aerosol monitor manufactured by TSI® Inc., Shoreview, MN, USA. The SidePak is lightweight and designed to be worn on the user's belt.

Abbreviations

APHEA	Air Pollution and Health: A European Approach
CF	Canadian Forces
COPD	Chronic Obstructive Pulmonary Disease
CVD	Cardiovascular Disease
DFHP	Director Force Health Protection
DHHAT	Deployable Health Hazards Assessment Team
DND	Department of National Defence (Canada)
DPS	Deployable Particulate Sampler
FHP	Force Health Protection
LPM	Liters per minute
μg	microgram
mg	milligram
$\mu g/m^3$	micrograms per cubic meter
mg/m^3	milligrams per cubic meter
NAAQS	National Ambient Air Quality Standards
PM	Particulate matter
PMCC	Pearson Product Moment Correlation Coefficient
USACHPPM	US Army Center for Health Promotion and Preventive Medicine
USEPA	United States Environmental Protection Agency

Chapter 1
Introduction

Statement of Problem

Aerosol particulate matter has existed for millennia and harmful effects from aerosol exposures have long been known, particularly from exposures related to mining (Agricola, 1556) and in many industries of the Industrial Revolution (Hunter, 1978). Only recently, have scientists begun to better comprehend the complexity of health effects related to both short and long term aerosol exposures.

Airborne particulate matter (PM) includes both solid particles and liquid droplets suspended in a gaseous medium. Atmospheric PM occurs both naturally and anthropogenically and exists in a wide range of sizes (NAAQS, 2006). Airborne PM with an aerodynamic diameter ≤ a nominal value of 2.5 μm ($PM_{2.5}$) is postulated to pose the largest health risk because, by sedimentation, these particles can migrate deeply into the lungs (EPA, 2008). Airborne particulate matter with an aerodynamic diameter ≤ a nominal value of 10 μm but >2.5 μm (PM_{10}) poses a health concern because these particles ostensibly accumulate in the upper respiratory tract and may cause illness. Both $PM_{2.5}$ and PM_{10} can exacerbate illnesses in those persons with pre-existing medical conditions (EPA, 2008).

A review of epidemiological studies has linked increased respiratory infections to airborne PM (Brunekreef and Forsberg, 2005). Epidemiological studies have associated exposure to airborne PM with an increase in respiratory

and cardiovascular disease (CVD), particularly with exposure to $PM_{2.5}$ (Peng, *et al*., 2008). However, other studies on long and short-term exposures to $PM_{2.5}$ and PM_{10} are inconclusive. Some studies have linked CVD, asthma, and chronic obstructive pulmonary disease (COPD) to increased mortality and morbidity (Brunekreef and Forsberg, 2005). The long-term effects of all possible exposures to airborne PM are unknown and study findings are mixed, but there is sufficient concern to warrant further investigation, particularly when chemicals are adsorbed to the particles or biological material is a component in the respirable fraction of air (Vincent, 2007). Mineral characteristics, sorptive properties, and the nature of mineral aerosol surfaces, are also important in determining the toxicity and carcinogenicity of a particle (Guthrie, 1997; Oberdoster, *et al*., 2005; Tran, *et al*., 2000; and Vincent, 2007).

Demographically, military personnel differ in physical health from the civilian population in so much as they are generally young and healthy. Military recruits are medically screened before admittance into the military, and during enlistment personnel have access to medical treatment facilities. However, of concern to the military are the potential effects that may manifest in personnel exposed to airborne PM during military operations. Studies completed on veterans of the Persian Gulf War have not shown any long-term effects to date. The study conducted by Richards, *et* al., to evaluate infectious disease threats to military personnel deployed to the Persian Gulf consisted of quantitative and qualitative determinations of quartz and other chemical constituents as well as individual particle size, shape, and elemental composition. Additionally, bacterial and

fungal cultures of sand samples were analyzed. An epidemiological survey of personnel for sore throat, cough, chronic rhinorrhea, and inability to work combined with the results of the studies concluded that the relatively brief exposure of the personnel did not result in an increase in upper respiratory symptoms. The study also suggests a low risk of subsequent disease because the proportion of concentrations of respirable quartz particles present in soil samples collected were very low; however, airborne PM were not studied (Richards, *et.al*., 1993). A study by Kelsall, *et al*., using respiratory examination, and spirometric testing did find that personnel reported more respiratory symptoms than a comparison group from the effects of exposure to oil fire smoke and dust storms. However, the results do not suggest any long-term sequelae from the exposure (Kelsall, *et al*., 2004). The findings may be attributable, in part, to the fact that the exposed personnel were generally healthy adults and if there are any detrimental health effects from exposure these may take decades to manifest (Richards *et al*, 1993; Guthrie, 1997; and Kelsall *et al*, 2004).

Environment Canada and the Canada-wide Standards for airborne PM exposures specify air quality and exposure limits in Canada. Current Canada-wide standards for $PM_{2.5}$ are 30 μg/m^3 per 24-hour averaging time. The standard for PM_{10} is under review and although there is evidence of health affects due to coarse PM, the Joint Action Implementation Coordinating Committee has found insufficient data to permit a recommendation. The Canadian Council of Ministers of the Environment may revisit the question of whether or not to develop a Canada-wide standard for coarse PM in 2010 (JAICC, 2005). The United States

Environmental Protection Agency (USEPA) National Ambient Air Quality Standards (NAAQS) established a 24-hour limit for $PM_{2.5}$ at 35 μg/m^3 and a limit of 150 μg/m^3 for PM_{10} (EPA, 2008).

Given the importance of health risk data, the effectiveness and accuracy of equipment used for the collection of health risk data are essential to the Canadian Forces (CF). To evaluate potential health risk for the exposure of deployed service members to airborne PM the Director Force Health Protection (DFHP) acquired both gravimetric and photometric aerosol samplers for assaying airborne PM. The gravimetric instrument is the SKC® Deployable Particulate Sampler (DPS), while the TSI® DustTrak™ 8520 (DustTrak) and Sidepak™AM510 (SidePak) are photometric aerosol monitors. If the data from the photometric instruments can be directly compared to data produced by the well-understood gravimetric approach, interchangeable use of both types of aerosol samplers would be possible with mission parameters and collection criteria determining which type would be most suitable. Establishing a strong link between each measurement method would allow for compilation and exchange of data between health risks advisors, regardless of the instrumentation used to collect the exposure data.

In the past, the CF Deployable Health Hazards Assessment Team (DHHAT) deployed the Airmetrics Minivol™ system but ceased its use in favour of the DPS during the last technical assistance visit to Afghanistan in 2005. The United States Army Center for Health Promotion and Preventive Medicine (USACHPPM) has performed validation studies on the Minivol and the DPS

instruments and the results determined a 0.98 correlation factor between the Airmetrics MiniVol™ and the DPS (Trakumas, *et al*., 2005). The DHHAT currently deploys the DPS because of this correlation with the Minivol as well as its portability and ease of use.

Sampling for PM_{10} is often used for measuring PM exposure in the field. However, there is significant interest in $PM_{2.5}$ because of its causal link to adverse health effects. Future considerations may require $PM_{2.5}$ sampling in lieu of, or in addition to, PM_{10} sampling for this reason. It is therefore necessary to evaluate and validate the ability of the instruments in the DHHAT inventory to determine if they meet effectiveness, suitability, and performance requirements at both the $PM_{2.5}$ and the PM_{10} levels in an operational environment. Depending upon the determinations, the instruments may be independently operated, and comparable data at both PM levels will be of value in health risk assessment. To date there are no studies or published data to show the comparability of data between these instrument types.

Hypothesis

The hypothesis of this research is that comparable environmental sampling results are obtained using either the gravimetric SKC® Deployable Particulate Sampler or the photometric instruments: the TSI® DustTrak™ 8520 and Sidepak™AM510 aerosol monitors, at the 2.5 and 10 µm aerodynamic diameter cut-points.

Research Aims

Specific aims of this research were to: collect $PM_{2.5}$ and PM_{10} ambient air sampling data using the DPS, DustTrac, and SidePak systems, compare the gravimetric and photometric particle count instruments to establish if a relationship between data can be obtained from each type of instrument, and evaluate the effectiveness, suitability, and performance of the systems in a desert environment.

Limitations of Study

Data obtained from simultaneous operation of the DPS and the DustTrak, and the DPS and SidePak instruments were desired. The instruments studied were operated concurrently and in close proximity to each other.

It must be taken into account that the sampling inlet design, the entrance shape, and flow rate through the inlet can affect sampling efficiency at each cut-point (Spurny, 1998).

The DPS is a gravimetric sampler that uses inertial impactor sampling technology. A limitation of gravimetric samplers is the possibility that the 2.5 μm and 10 μm cut-points may permit smaller particles to be impacted on the filter. However, current technological advances in aerosol filtration have reduced this possibility considerably (Johnson, *et al*., 2003; SKC, 2006; and Spurny, 1998).

The DustTrak and SidePak use light scattering technology to determine mass concentration in real-time. Photometric instruments can also permit particles smaller or larger than the cut-point to be erroneously counted. For

example, particles may be counted because of spatial orientation, particle composition, or aerosol concentration and alter the light scattering that will introduce an error (Johnson, *et al*., 2003 and Vincent, 2007). Calibration constants corresponding to a different type of aerosol such as coal dust or oil mist can be changed using the procedure outlined in the DustTrak manual. In addition, it is recommended by TSI that the instruments be returned to the factory for cleaning and calibration on an annual basis (TSI, 2007).

The DPS has a flow rate of 10 liters per minute (LPM) (14.4 m^3/ day) versus 1.70 LPM (2.40 m^3/day) for the photometric instruments. The USEPA recommends 15.2 m^3/day as it approaches the daily average human inhalation rate of 22.0 m^3/day (EPA, 1999). From the manufacturer's literature, it was assumed the geometry/velocity combination admitted the specified cut-point and both types of instruments would be comparable. Both the photometric and gravimetric instruments use a precise and accurate flow rate to ensure that particles are drawn in at specific rate to obtain the specified cut-point.

Evaluation of the PM weight used a Mettler MT5 microbalance (Mettler-Toledo, Inc., 1990 Polaris Parkway, Columbus, OH). The MT5 has accuracy limitations of (+/-) 0.015 mg and may mask a true difference in the data when measured values approach this value. Careful calibration of the balance before weighing and care in handling the filters will mitigate filter weight inaccuracies. Handling the filters in the field environment may cause contamination or damage, potentially introducing a measurement error.

Unknown fluctuations of humidity and temperature in the filter-conditioning chamber could influence the confidence of the filter weights. Even small variances in the chamber humidity can significantly affect the filter weights. Heat and humidity control appliances, as well as access control are used to maintain a constant environment for filter weighing.

Field sampling reduces the ability to control for many of the exigent parameters for which the systems are subjected, such as: spatial PM concentration variation, wind, precipitation, humidity, atmospheric pressure, heat, and cold. In order to control for this a relatively environmentally stable location was selected for the sampling.

Chapter Two
Literature Review

Aerosols

An aerosol is defined as PM, which is a solid or liquid droplet larger than a molecule, but small enough to remain suspended in the atmosphere. Natural sources include salt particles from sea spray, dust and clay particles, and particles from volcanic activity carried by the wind. Anthropogenic aerosols derive from vehicles, combustion industries, and nuclear incidents intentional or not (CEPA, 1999). In the atmosphere, aerosols are nuclei for the condensation of water droplets and ice crystals. They participate in various chemical cycles, and absorb or scatter solar radiation to influence the Earth's radiation budget (NASA, 2004). Aerosols are comprised of several species defined as: dust, fumes, fog, smokes, mists, sprays, and these can contain particles of minerals, spores, viruses, and chemicals. There are numerous medically beneficial aerosols, such as inhalers for people suffering from asthma; however, many human generated aerosols are considered pollutants (Vincent, 2007).

Determination of particle morphology is by size, shape, and appearance. Airborne PM of concern in this study are defined as fine PM (particles $\leq PM_{2.5}$) and coarse PM (particles $\leq PM_{10}$ but $\geq PM_{2.5}$). There are other particles, that were not included in this study, and they include particles in the 0.1 μm to ultrafine (<100 nm diameter) range such as nanoparticles, chemicals, and endotoxins. Particle shape can be either isometric or non-isometric. Isometric

particles have length dimensions independent of their orientation and their shape in a single dimension. For example, the measurable dimension of a spherical particle is the diameter. Liquid droplets and metal fumes are spherical due to the influence of liquid surface tension. Bioaerosol particles such as allergenic pollens and dust mite fecal pellets are considered spherical or essentially spherical. Non-isometric particles are ellipsoids, defined as particles where length exceeds the diameter by a ratio ≥ 3:1. Non-isometric fiber particles occur frequently in industrial aerosols, such as asbestos, metal filings, carbon and vitreous fibers, and their composites (Johnson, *et al*., 2003). Dust particles produced during grinding, pulverization, or sanding operations and some crystalline particles are considered isometric even though they are not exactly spherical in nature.

Aerosols consisting of single particles, as opposed to aggregate particles, are of the greatest concern to human health as they are easily inhaled and can accumulate in the lungs. Single particles include both isometric and non-isometric particles. Particles that are spherical may be defined by geometric diameter.

In aerosol aerodynamics, particles such as dust are defined as having an aerodynamic diameter, which is a physical property of the particle in air. These particles may have irregular shapes with actual geometric diameters that are difficult to measure, but the aerodynamic diameter expresses the particle aerodynamic behaviour as if it was spherical with a density of 1.0 mg/cm^3 (Vincent, 2007). As aerodynamic diameter is based on particle behaviour

instead of absolute density, the use of aerodynamic diameter allows one to predict where in the respiratory tract particles may deposit regardless of their shape, actual size, or density (Dallas, 2000).

Aggregate particles form when initial concentrations of particles are in the order of 10^6 particles/cm^3. Commonly the particles range in diameter from 1 nm to 0.1 μm, and coagulate or flocculate to form aggregates. Soot particles formed by the incomplete combustion of hydrocarbons are an example. The coarse dimensions of these particles have their own specific characteristics and the increased surface area can retain molecules from condensation or as vapours, and through catalytic reaction can produce new gaseous species (Johnson, *et al*., 2003).

Deposition Mechanisms

An important deposition mechanism in aerosol sampling involves Newton's First Law of Motion. Newton's First Law states: that every object will remain at rest or in uniform motion in a straight line, unless compelled to change its state if acted upon by an external force. In the context of aerosols, when the aerosol stream is forced to change direction suddenly, the particle's momentum will carry it across airflow streamlines before its momentum in that direction is depleted by fluid drag or impaction (Spurny, 1998). The probability of impaction increases with the mass and velocity of the particle and varies depending on the degree of vector change. Therefore, if a particle enters a measurement instrument or the respiratory tract in an area of high velocity and there is a change in direction, the particle may traverse the airflow streamlines and impact. If it is unable to,

because of distance for example, then the particle re-enters the airflow and continues (Hinds, 1999 and Esmen, 1996). Once particles are inhaled into the body, they are affected by several processes and deposit according to size within the respiratory system.

Sedimentation pertains to particles of various sizes ranging from suspensions of dust and pollen to mists, fogs, and fibers. Sedimentation of particles is the process by which particles collect or deposit on solid surfaces, thus decreasing their concentration in the air. The rate of sedimentation depends on the morphology of the particle, orientation for non-spherical particles, air density, and viscosity. The mechanisms of deposition are most effective for very small or very large particles. Very large particles settle out through sedimentation or impaction and very small particles are influenced by Brownian motion, seemingly random movement of particles suspended in a liquid or gas, and agglutinate until they achieve a diameter of approximately 0.3 μm, at which time they may deposit on tissue surfaces. This has a great influence on the amount of $PM_{2.5}$ in the air and particle deposition in the respiratory tract (Johnson, *et al*., 2003).

Aerosol particles suspended in a gaseous medium are in constant collision with individual gas molecules and this causes the smaller particles to undergo random translational motion due to molecular collisions and random displacements known as diffusion. The Brownian motion gives rise to the diffusion of particles in accordance with Fick's Law of classical diffusion; the net motion of diffusion from an area of high concentration to an area of low

concentration. Small particle diameter, large concentration differences, and short distances characterize diffusive transport (Johnson, *et al*., 2003).

Interception is the process of an aerosol flowing past a collecting surface resulting in particle deposition. The process is similar to impaction except interception occurs when the side of a particle tangentially contacts the surface of a turn or obstacle that it is unable to negotiate. Attenuation of elongated particles is more likely to occur than for spherical or nearly spherical particles of equal mass due to particle length (Johnson, *et al*., 2003).

Various forces act upon particles contacting surfaces. Some enhance retention and others repel or re-suspend the particles from the media. Electrostatic forces, negative or positive charges imparted on a particle, promote the retention of particles. Capillary forces promote retention due to the adsorption of a liquid film between the particle and the surface. Forces that tend to dislodge deposited material are those related to vibration and air currents; smaller particles are more difficult to dislodge than larger particles (Hinds, 1999 and Esmen, 1996).

Filtration and Sampling

Filtration of aerosols permits the study of aerosol mass concentrations, count concentrations, particle morphology, radioactivity, chemical composition, and biological hazards. A variety of different media is available and the type used depends on what the investigator is attempting to measure, the characteristics of the aerosol, and the analytical technique to be used.

Fibrous filters are a complex mesh and may be made of cellulose, glass, or quartz filaments that are weaved to form a dense media to which particles deposit by gravitational settling, impaction, interception, diffusion, and electrostatics.

Fibrous filters are inexpensive and have a high load capacity. They are subject to humidity interference and have high mechanical strength. The filters are fragile and care is required when placing and removing the filter on the cassette (Vincent, 2007).

Membrane filters are characterized as thin sheets of a gel material that consists of interconnecting pores through which air may pass. The aerosol laden air travels internally through a convoluted route of successive pore-like elements, stripping particles from the air that are too large to pass though with the airflow. Gels can be composed of cellulose ester, nylon, polyvinyl chloride, or polytetrafluoroethylene. The Nucleopore® filter, is a special form of membrane that has holes a few micrometers in size that are created by exposing the plastic, such as polycarbonate, to neutron bombardment and subsequent etching. Radiation weakens the plastic and creates areas that are removed chemically to create holes of uniform diameter. Unlike micropore filters, the nucleopore filters allow for an even distribution of a collected sample in one plane across the exposed surface (Vincent, 2007).

Granular bed filters are a third category of filter. They are comprised of granular material such as charcoal, glass, quartz, or metals that are packed onto a sheet and sintered to form a permanent structure. Thin disks of silver granules

sintered in this manner are referred to as silver membrane filters. This type of filter is used for corrosives and high temperature sampling (Vincent, 2007).

Aerosol Measurement

Aerosol sampling involves inspiring a volume of air/gas by means of a pump via an orifice into a unit that contains sensors, filters, or other substrates. The rationale for sampling is to acquire information with regard to existing aerosol properties over a given period. The separation of particles from the air mass enables the characteristic assessment of the particles by gravimetrics, particle count, microscopy, or assaying by other techniques. The most common measurement of an aerosol is mass concentration, which is the mass of the PM per unit volume of air, expressed in micrograms or milligrams per cubic meter ($\mu g/m^3$ or mg/m^3). To determine other aerosol properties investigators use analytical instruments to measure quantity, surface area concentrations, distribution of particle sizes, and biological or chemical composition (Vincent, 2007).

Aspiration of the particle into the sampler is highly complex and depends on sampler characteristics, the ambient environment, and the particle's aerodynamics when entering the sampler. Airflow and particle behaviour surrounding and within the sampling area are critical issues when assessing the sampling characteristics of the device. It is imperative that aerosol sampling is performed in such a manner as to capture the desired size particles (Spurny, 1998).

The two types of instruments used in this research were gravimetric and photometric. Sampling with the gravimetric instrument involves drawing an aerosol sample into the instrument and through separation and filtration, the PM is deposited onto a filter. Subsequent analysis of the captured sample is completed at a laboratory (Spurny, 1998). Photometric instruments inspire a volume of air or gas into the instrument and through photodetection, the PM in the aerosol sample is estimated. The data are recorded electronically during photometric measurement and usually the results are immediately made available (Chen and Pui, 2008). The following information was obtained from the manufacturer's literature, manuals, and sales information.

The DPS System is a compact, portable particulate sampler with an all-in-one design and is powered by a rechargeable lithium ion battery. The system is comprised of the Leland Legacy® sample pump, an IMPACT sampler, connecting tubing, mounting bracket, impactor cap, spare filter cassette, and laminar flow meter with battery pack, battery charger, calibration adapter, impaction substrate disks, and a filter cassette opener. The entire system is ensconced in a ruggedized case (Pelican™ Products, Inc., Torrance, CA), and is designed to operate securely inside the case after initial set-up. The system is able to sample at 10.0 LPM for 24 hours on a full battery charge. Changing the impactor inlet enables sampling for either $PM_{2.5}$ or PM_{10} (SKC, 2006).

The DustTrac is a portable battery operated laser photometer. The system is comprised of a 10mm Nylon Dorr-Oliver Cyclone, conditioning kit 1.0 and 2.5 µm, sampling extension tube, and service tools. The entire system can be

enclosed in a ruggedized case (Pelican™ Products, Inc., Torrance, CA), and is designed to operate securely inside the case after initial set-up. The system is able to sample PM 0.1, 2.5, and 10, for 16 hours at 1.7 LPM (TSI, 2002).

The SidePak is a portable battery operated belt-mountable (personal monitor) laser photometer. The system allows the operator to select aerosol inlet conditioners with a respirable cyclone, or one of three integrated impactors. The system consists of a 10mm Nylon Dorr-Oliver Cyclone, conditioning kit 1.0 and 2.5 µm, sampling extension tube, and service tools. The system is able to sample PM 0.1, 2.5, and 10, for 22.5 hours on an alkaline battery pack at 1.7 LPM (TSI, 2002).

Pumps

A necessity of all pumps used for quantitative air sampling is that they deliver a specific flow rate that is constant and consistent over a definitive period. The correct flow rate and accurate measurement are critical to optimizing the performance of the size-selective sampler. A properly functioning pump is also necessary in determining the air mass volume aspirated during the sampling period; this enables the conversion of mass PM to mass concentration (Dietrich, 2003).

The SKC Leland Legacy® sample pump used with the DPS is a vacuum style pump that provides flow rates from 5 to 15 LPM. It is a compact, portable and battery operated device. The pump uses a lithium ion battery that provides a 24-hour run time when using an impactor and other sampling devices with low backpressures. It is suitable for internal and external environments. The pump

has a patented internal flow sensor that measures flow directly and acts as a secondary standard to maintain airflow from initial start-up. Built-in sensors that compensate for differences in temperature and atmospheric pressure during sampling automatically maintain a constant airflow velocity (SKC, 2006).

The DustTrak and SidePak photometric instruments have an integral pump that is factory calibrated for volumetric flow. The DustTrak flow rate is user adjustable from 1.4 to 2.4 LPM. The SidePak has a flow range of 0.7 to 1.8 LPM and is user adjustable (TSI, 2002).

The calibration of an air sampling pump is mandatory for aerosol sampling to ensure the correct volume of air is inspired. The DryCal® DC-Lite from BIOS International Corporation (Butler, NJ), combines near frictionless piston technology with photo-optic sensing to obtain volumetric flow rates quickly and accurately. The unit is housed in a 5” x5” x 2.75 case and operates on AC/DC power (BIOS, 2000).

Medical Impact of Particulate Matter Exposure

Acute and chronic exposures to aerosol PM are known to have detrimental health effects. The potentially harmful and adverse properties of PM can affect personal readiness levels and the ability to accomplish military missions due to illness. A person’s primary route of exposure to PM is through inhalation and secondarily through ingestion. Aerodynamic diameter is an important parameter that allows for the prediction of where in the respiratory system the particles will deposit. An understanding of the body’s defence mechanisms, physiological response, and the particles characteristics allows one to predict the potentially

harmful or lethal effects within the body (Alexander and Still, 2008 and Johnson, *et al*., 2003).

The most important properties concerning inhaled particle deposition and potential toxicity are particle size, morphology, hygroscopicity (water vapour absorption tendency), number, and mass concentration, surface area of the tissue, and the type of particle and its electrical charge. Integration of these factors will contribute to the capture, entrainment, and deposition of aerosol PM. The human body defends against inhaled PM in three congruous but anatomically different regions of the respiratory tract. The three regional divisions are the nasopharyngeal, tracheobronchial, and the pulmonary regions. The inhalable fraction of respirable aerosols involves all three regions (Johnson, *et al*., 2003).

Air is inhaled into the respiratory system via the nasopharyngeal region. The nasopharyngeal region traps large particles ≥ approximately 10 μm. As air enters the nose it encounters a moist and turbinated region that is initially lined with hairs. Air entering the nose is partially filtered and almost completely humidified before it passes into the pharynx. Particles consisting of hygroscopic material can absorb significant amounts of water in the nasopharyngeal region, due to the humidity, and have difficulty traversing the convoluted passages because of the increase in size. As air is inhaled, it encounters obstructions and directional changes. Particles suspended in the air, having greater mass and momentum than the air cannot navigate around the obstructions. Linear momentum causes these particles to impact on the nasal mucosae and become

entrapped in the mucous coating (Guyton and Hall, 2000). Particles < 10 μm and those larger particles not captured in this region flow into the tracheobronchial region.

The tracheobronchial region is a branched section consisting of 16 divisions lined with mucosae and ciliated epithelium. The function of this region is to distribute air quickly and evenly to the lungs. The airway diameter decreases with each succeeding division but the number of airways increases geometrically. This results in a decrease in airflow velocity from approximately 200 cm/sec down to about 3 cm/sec in the terminal bronchioles. Transit time, or the time of particle residence, lengthens from approximately 0.01 seconds in the larger bronchi to 0.1 seconds in the terminal bronchioles. In the upper tracheobronchial divisions, inertial impaction of particles is the primary deposition mechanism due to the high air velocity and larger airway diameters. As the respiratory passageways decrease in diameter and velocity distally, the deposition of particles by sedimentation and diffusion are more prevalent (Johnson, *et al*., 2003).

The mucociliary escalator is a clearance mechanism within the nasopharyngeal and tracheobronchial regions. The surface areas of those regions are lined with ciliated epithelium cells that project 200 to 300 cilia per cell. The cilia beat in a coordinated fashion to move particles trapped in the mucous toward the pharynx where it is expectorated or swallowed (Guyton and Hall, 2000). Mucociliary clearance is usually accomplished within 2 - 48 hours (Dallas,

2000). Small particles typically < 5 μm, and any larger particles that were not trapped, travel to the pulmonary region.

The pulmonary region contains respiratory bronchioles, alveolar ducts, and the alveoli where the gas exchange takes place. The air velocity drops from about 1 cm/second to less than 0.1 cm/second in the alveolar ducts and the residence time increases to more than 1 second. Depending on particle size, sedimentation, or diffusion is the dominant deposition mechanism. Sedimentation of particles > 1.0 μm occurs as particles descend lower into the bronchiolar tree. This is due to the effects of gravity, distally decreasing passage diameters, and negligible velocity. Ultrafine particles, particles ≤ 1.0 μm, exhibit significant diffusion in the pulmonary region and may deposit in large numbers on the delicate membranes of the alveolar tissue (Dallas, 2000). Although these particles make up only a small fraction of the total mass they may cause severe or fatal injuries due to the type of particles, the particle's position in the pulmonary region, or toxins adhered to the particles (Johnson, *et al*., 2003). Any increase from the normal respiration activity at rest, such as: running, mouth breathing, or heavy exertion will increase the amount of particles entering the respiratory system. Those ultrafine particles that do not deposit in the pulmonary region are exhaled from the body.

Deposition of airborne particles on or in the body can exert undesirable local and systemic effects by aggravating an existing disease or inducing a disease. The factors influencing toxicity with pulmonary exposure are concentration, solubility, respiration rate, length of exposure, integrity of the respiratory tract and

particle size (ATSDR, 2007). These factors can act locally to aggravate lung diseases such as asthma and COPD or can be implicated as inducing disease such as cancer.

Systemic diseases can be affected by the physical and chemical processes through which a substance is absorbed or eliminated. When a substance is absorbed, the concentration, size, chemical structure, and lipid solubility directly relate to residence time in the tissues and organs (O'Flaherty, 2000). Particle absorption, distribution, biotransformation, and excretion (ADBE) processes greatly influence physiological response. The ADBE processes refer to the quantitative time that toxins exert their effects on the body and the process is influenced by factors such as age, gender, and ethnicity (ATSDR, 2007).

Absorption of PM into the body is primarily through inhalation and secondarily through ingestion. Inhaled aerosols and toxins can directly affect the lungs where they can be readily absorbed (ATSDR, 2007). Ingestion can occur when contaminated food or water are swallowed. Ingestion of contaminant occurs when the mucociliary escalator transports contaminated material to the pharynx and it is swallowed.

Distribution of ingested or inhaled PM, and chemicals desorbed from particles, is effected by particle fat solubility, polarity, molecular weight, and size. These properties govern the distribution of the substance throughout the body, but also its penetration into the cells and tissues. Lipophilic toxins are retained in fatty tissue and are difficult for the body to eliminate, increasing the likelihood of the accumulation of hazardous substances. However, lipophilic compounds can

biotransform into hydrophilic compounds that are more readily excreted in the urine and therefore, are less likely to accumulate (Yuill, 2008).

Biotransformation is the chemical interaction with enzymes, proteins, and chemicals in the body. Biotransformation in the liver or kidneys occurs when PM reacts with enzymes or chemicals in the body that can detoxify or increase the particles toxicity. Highly reactive metabolites can interact with cellular macromolecules such as DNA. In occupational environments, vinyl chloride may adsorb to PM and cause a serious health affect (Spectrum, 2009). The biotransformation of vinyl chloride to vinyl chloride epoxide allows it to bind with DNA and RNA, which can lead to angiosarcoma, a rare form of liver cancer (Yuill, 2008). The liver metabolizes many harmful substances that are absorbed from the gastrointestinal tract and excretes them into the bloodstream or they are excreted as metabolites in the bile before they can enter the circulatory system. The bile is subsequently excreted into the gastrointestinal tract and some may be reabsorbed or is eliminated from the body as feces (O'Flaherty, 2000).

Excretion is the elimination of xenobiotics from the body whereby they are expelled via urine, feces, sweat, tears, or exhalation. The kidneys excrete a large number of compounds that it filters out of the bloodstream and functions to eliminate most of the body's liquid waste, including hydrophilic toxins. The lungs are a vital organ for the excretion of gases that may have accumulated in the body (O'Flaherty, 2000).

Epidemiology

Airborne PM is found in a wide range of environments and can pose a significant health risk. Epidemiological evidence finds acute and chronic exposure to $PM_{2.5}$ and PM_{10} can cause acute and chronic illnesses, particularly in individuals with pre-existing medical conditions such as asthma or COPD. The particulates can cause irritation, inflammation, and exacerbate chronic and latent cardiovascular and respiratory diseases leading to an increase in morbidity and mortality rates (Pope III, *et al.*, 2002 and Zeger, *et al*., 2008). The potential for latent effects of airborne PM exposure after the Persian Gulf War of the 1990's prompted a number of studies. The study of the latent effects of PM continues, but is confounded by conflicting acute and chronic respiratory illness studies to which the findings are inconclusive and inconsistent (Winkenwerder, Jr. W., 2002). The latent effects from airborne PM in the Persian Gulf War and operations currently being conducted in Southwest Asia may not manifest for decades. Current and emerging studies are also investigating the toxic effects derived from ultrafine, fine, and coarse PM to clarify their deposition and translocation mechanisms (Alexander and Still, 2007).

Epidemiological studies have linked both $PM_{2.5}$ and PM_{10} to increased cardiovascular and respiratory morbidity and mortality, especially among the elderly and those with pre-existing medical conditions. Various studies report inconclusive findings, and caveats such as size of study, time of year, or geographic location are commonly cited. For example, Brunekreef and Forsberg reported that localities in their meta-analysis with high incidence of anthropogenic

or natural air pollution tended to have increased incidence of morbidity and mortality with regard to cardiovascular and respiratory disease, but this was dependant on airborne PM size and geographic location (Brunekreef and Forsberg, 2005). A study by Hendryx associated higher chronic heart, respiratory, and kidney disease mortality in coal mining areas of the Appalachian region compared to non-Appalachian regions. He proposed the association of disease may reflect environmental exposure to PM or the toxic agents found in coals that are released in mining and processing (Hendryx, 2009).

In the Harvard Six Cities studies, both the original (1979 to 1989) and the follow-ups (2001 and 2006) found total cardiovascular, respiratory, and lung cancer mortalities were each positively associated with ambient airborne $PM_{2.5}$ concentrations (Laden, *et al*., 2006). In addition, the 2006 follow-up study showed a reduction in ambient $PM_{2.5}$ concentrations was associated with a reduced mortality risk, thus verifying results from the previous Harvard Six Cities study as well as numerous other studies (Laden *et al*., 2006). It has been suggested toxicity is associated with ultrafine and fine airborne PM exposures as these particles can readily deposit in the lungs (Anderson, *et* al., 2001). Studies by Pope III, *et al*., Zeger, *et al*., and a multitude of other researchers have found similar results associating fine PM and cardiovascular and respiratory disease with increased morbidity and mortality (Pope III, *et al*., 2002 and Zeger, *et al*., 2008). The findings for $PM_{2.5}$ are more definitive than the findings for PM_{10}, which are conflicting and inconclusive.

A compendium of studies has found evidence that exposure to coarse airborne PM has adverse effects on health. Equally, there is a compilation of data refuting this claim. Analyses that are restricted to particular ailments such as CVD and upper respiratory tract infections (URTI) find an association with exposure to either fine or coarse PM, but not both, when both are being sampled. The studies are principally from regions such as Coachella Valley, California; Phoenix, Arizona; Mexico City, Mexico; and from some regions in Canada. The study in Coachella Valley found evidence for the effects of fine airborne particles on mortality, but not coarse particles. When the study was restricted to cardiovascular mortality, a significant association was found with coarse airborne PM but not fine PM (Ostro, 2000). The Air Pollution and Health: a European Approach 2 (APHEA 2) study of 1998, a follow-up to the APHEA project of 1993, positively associated exposure to airborne PM_{10} with an increase in hospital admissions for respiratory disease, COPD and asthma in eight European cities (Atkinson, *et al*., 2001). Conversely, Peng, *et* al., found no statistically significant association between coarse particulates and hospital admissions for cardiovascular and respiratory disease using a database of 108 United States counties after adjusting for exposure to airborne $PM_{2.5}$ (Peng, *et* al., 2008).

Studies in areas afflicted with dust storms and wind-blown dust also have mixed results. A temporal series of mortality data from Spokane, Washington found there was no increased respiratory mortality rate on dust storm days that had an average airborne PM_{10} concentration of 263 $\mu g/m^3$compared to control

days in which the mean PM_{10} concentration was 42 μg/m^3 (Schwartz, *et* al., 1996). A hospital admissions study from the state of Washington did however find an increase in hospital admissions associated with exposure to airborne PM_{10} (Hefflin, *et* al., 1994), while a study in Anchorage, Alaska, found significant effects of airborne PM_{10}, consisting of coarse crustal material, for asthma, bronchitis, and URTI on outpatient visits (Gordian, 1996). Research remains conflicted as to the association between morbidity, mortality, and PM_{10}. The current studies for airborne PM_{10} are becoming less frequent due to the belief that airborne $PM_{2.5}$ poses the greater health risk. There is a possibility that monitoring of PM_{10} may be replaced by the monitoring of $PM_{2.5}$; some advocates believe money and research should be focused solely on $PM_{2.5}$ (Anderson, *et al*., 2001).

Atherosclerosis is an underlying cause of some cardiovascular diseases and it has recently come under investigation as there is evidence linking it to airborne PM exposure. The findings of research regarding exposure to airborne PM and its relationship to subclinical atherosclerotic disease have results mirroring those of other studies concerning cardiovascular and respiratory illnesses. Atherosclerosis is the major underlying pathology of CVD and is a chronic inflammatory response within the walls of arteries caused primarily by the accumulation of macrophage white blood cells and promoted by low-density lipoproteins (Guyton and Hall, 2000). Three measures of subclinical atherosclerosis are the common carotid intimal-medial thickness (CIMT), coronary artery calcification (CAC) and the ankle-brachial index (ABI). In a study

carried out by Diez-Roux, *et al*., some evidence of association between airborne PM and CIMT was found, however the results for CAC and ABI were inconsistent (Diez-Roux, *et al*., 2008). A study by Hoffman, *et al*., achieved similar results and concluded exposure to airborne PM from residential vehicular traffic is associated with coronary atherosclerosis (Hoffman, *et al*., 2007). Further study in this area is warranted as volumes of traffic, urbanization, and industry increase.

Developments in science and technology regarding the significance of exposure to airborne PM have expanded dramatically over the past one hundred years. However, to better comprehend the dangers associated with PM investigators will require a multi-disciplinary approach. In the past, it was surmised particle toxicity was related to mass and that ultrafine and fine particle contribution to mass was negligible and therefore deemed insignificant to the etiology of health effects. Recent studies have shown this to be incorrect and ultrafine and fine particles can contribute significantly to health impacts (Alexander and Still, 2007). Research on the health effects of PM_{10} is inconsistent and inconclusive, whereas $PM_{2.5}$ data are more conclusive as it is more extensively studied. It is necessary to establish higher standards and improve methods to measure PM exposure to better assess the danger PM poses to human health. A comprehensive knowledge of the aerosol sampling instruments, their interoperability, and the continuation of airborne PM sampling and monitoring is vital to identifying potential hazards to which personnel may be exposed.

Chapter Three
Comparative Study

Abstract:

This study compared gravimetric and photometric aerosol sampling instruments for determining airborne concentrations of particulate matter. The instruments used were (1) the SKC® Deployable Particulate Sampler (DPS) that collects a sample on a filter, which is gravimetrically analyzed for concentration of mass, and (2) the TSI® DustTrak™ 8520 and Sidepak™AM510 that use photometry to estimate airborne particulate concentration. The capability to use these samplers interchangeably would permit employment of the best-suited instrument based on logistical and mission parameters for military force health protection. The instruments were deployed at Yuma Proving Grounds, Arizona for testing and were used in side-by-side sampling over a period of 13 days. Three statistical analyses, Pearson correlation coefficient, correlation within means, and the Bland-Altman analysis were used to compare the derived data. Statistical interpretation of the data between the DPS and the DustTrak at the PM_{10} cut-point found a strong correlation of data using the metric devised for this study measuring the strength of a relationship between two variables. Analytical comparisons for the DPS and DustTrak at the $PM_{2.5}$ cut-point demonstrated a weak relationship. The analysis between the DPS and the SidePak was not possible as the power source did not enable the Sidepak to sample for a twenty-four hour period and thus the samples collected were not comparable. A requirement exists for further laboratory and field studies.

Introduction

Exposure to airborne PM is associated with exacerbation and initiation of cardiovascular and respiratory disease. The possible harmful and adverse properties of PM can affect personal readiness levels and the ability to accomplish military missions due to illness.

A study was requested by the Canadian Forces Medical Services, DFHP, as part of Force Health Protection initiatives, to evaluate the comparability of aerosol samplers from two different categories for collecting/ measuring PM, gravimetric (SKC® Deployable Particulate Sampler) and photometric (TSI® DustTrak™ 8520 and Sidepak™AM510). Independently published and reviewed articles on the instruments could not be located. Establishing a positive correlation between the photometric methods and the widely accepted gravimetric approach will allow the compilation and exchange of data to mitigate potentially hazardous exposures. This will permit deployment of either instrument type depending on mission parameters and collection criteria with a high degree of confidence.

The samplers selected for this study measure airborne particles by either gravimetrics or by particle count utilizing photometric technology. The gravimetric sampler is an inertial impact sampler that efficiently removes particles larger than the cut-point by capturing them on a disposable oiled impaction substrate. The particles that are smaller than the cut-point are collected on a 47 mm filter (SKC, 2006). Photometric detection measures light scattering. The particles in the aerosol stream scatter light in all directions and a lens at 90^o to both the aerosol stream and a laser beam collects a fraction of the scattered light and focuses it

on a photodetector. The detector then converts the light into an electrical signal. The voltage of the signal is proportional to the amount of light scattered by the PM in the aerosol and the instrument provides results as mass concentration (TSI, 2002).

The DPS is the comparison standard for this study. Gravimetric sampling has few variables involved in volumetric sampling and has been studied extensively. The DPS and Airmetrics MiniVol™ gravimetric sampling systems are not USEPA approved as reference method instruments for particulate sampling; however, the Minivol is widely used and accepted. USACHPPM and SKC Inc. performed validation studies between the MiniVol and the DPS and the two instruments produced highly correlated data, r = 0.984, when sampling airborne PM_{10} (Trakumas, *et al*., 2005 and Engelbrecht, *et al*., 2008).

Two categories of airborne PM were assessed in this study, aerosol particles between 2.5 μm and 10 μm in aerodynamic diameter (PM_{10}) and particles less than or equal to 2.5 μm in aerodynamic diameter ($PM_{2.5}$). Testing was conducted for a total of 13 days and each sampling event covered a 24-hour period (or until battery exhaustion). The instruments were maintained in accordance with the manufacturer's operating and maintenance instructions and the batteries were changed every 24 hours.

Three statistical analyses were used to compare and contrast the data: the Pearson product moment correlation coefficient (PMCC), the correlation within means, and the Bland-Altman difference against means. The statistical analyses

describe the relationship between the instruments with respect to reported mass concentrations of airborne $PM_{2.5}$ and PM_{10}.

Materials and Methods

Particulate sampling was conducted at Yuma Proving Grounds, Arizona; a location with comparatively stable atmospheric conditions. During this work the diurnal temperature, barometric pressure, dew point, relative humidity, windspeed, and precipitation, remained relatively constant during the sampling period; except for two days of rain. Meteorological data obtained from the U.S. Marine Corp Air Station Yuma weather information (Weather Underground, 2008) showed that the average temperature for this period was 69.76^o F (low 55.76^o F, high 77.92^o F). The average atmospheric pressure was 30.00 in. Hg. Average dew point and relative humidity were 41^o F and 45% respectively. The windspeed varied from 1 mph to 14 mph with sporadic gusts averaging 19 mph (Figure 3-1). Measureable precipitation occurred on two days, for a total of 2.22 inches. The duration of the sampling was from 19 November 2008 to 04 December 2008 for a total of 13 days and each sampling period was 24 hours or, in the case of the SidePak, until battery exhaustion.

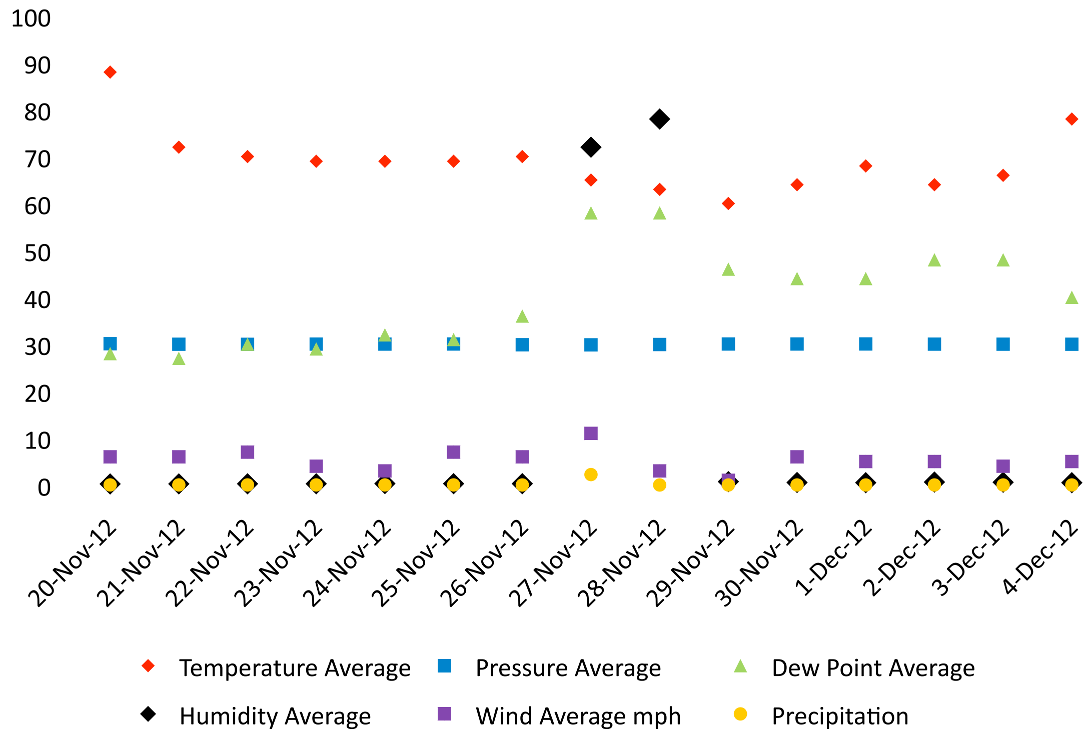


Figure 3-1. Weather data from Yuma Marine Corps Air Station, Arizona during the sampling period. The graph displays the average daily temperature, barometric pressure, dew point, relative humidity, windspeed, and precipitation.

The samplers were co-located at three stations, each station having one of each type of instrument (Figure 3-2). Daily rotation of the instruments from one site to the next ensured all received equal exposure at each of the three sites. The area used was the Patton Level Trails located at N32^{o}49.772’ W114^{o}24.059’. The three sites were located along a utility pole line and spaced 60 m apart. The samplers were affixed to utility poles at an inlet height of 182 cm and at a distance of 1.0 m between sampler heads. Mounting of the sampler inlets was to a bracket supplied by the manufacturer (DPS) or affixed to a strut (DustTrak and SidePak) (Figure 3-2). The samplers were maintained in the field

in accordance with the manufacturers' operating and maintenance instructions and the batteries were changed every 24 hours.

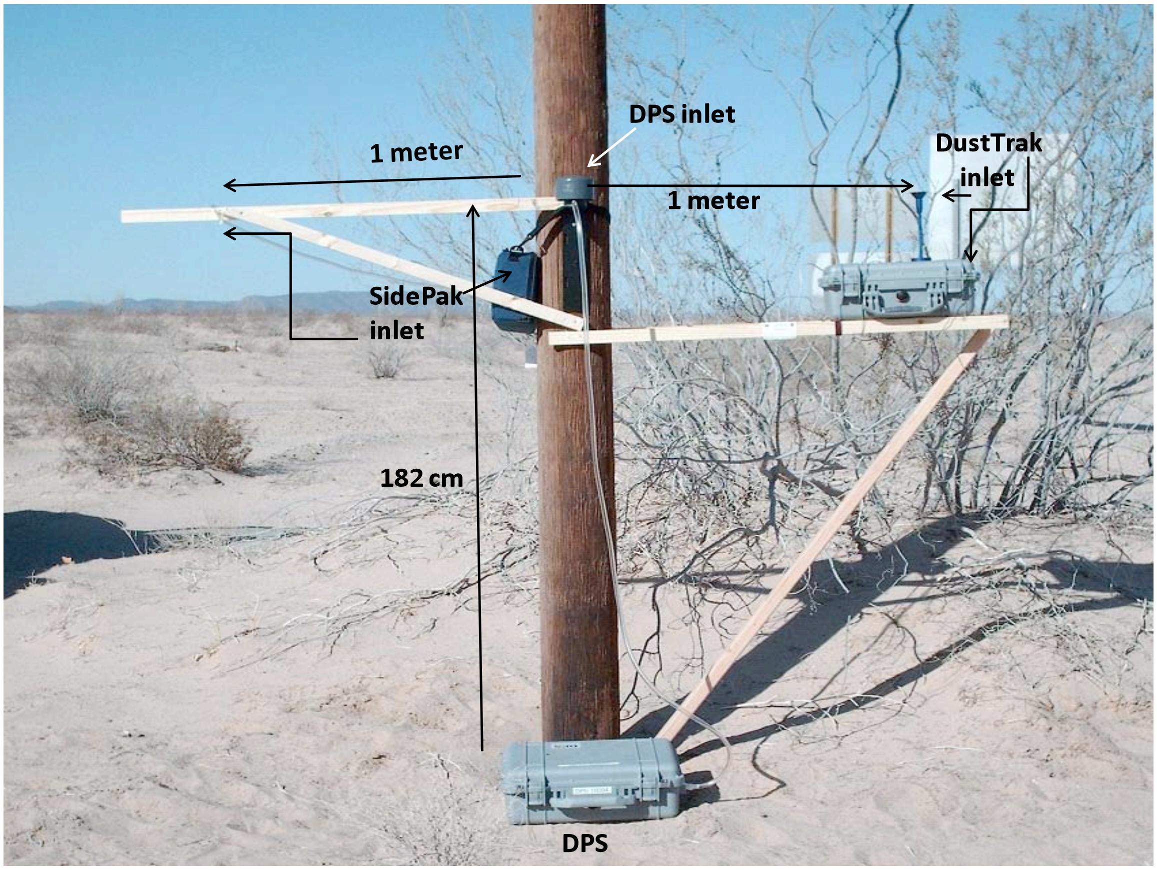


Figure 3-2. The SKC® Deployable Particulate Sampler, TSI® DustTrak™8520, and SidePak™AM510 deployed at Yuma Proving Grounds, Arizona.

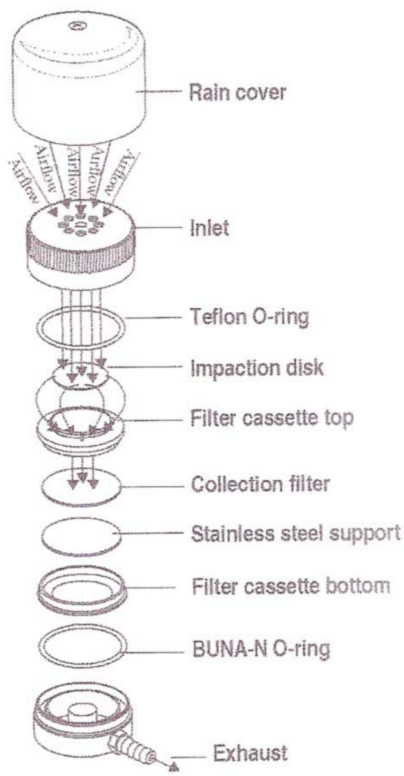
The SKC IMPACT sampler is a single-stage inertial impactor used for the efficient collection of $PM_{2.5}$ or PM_{10} in the DPS system from ambient air. A sampling pump operating at 10.0 LPM, calibrated before sampling, draws particles through an impactor designed to remove particles larger than the cut-point by capturing them on a disposable oiled impaction substrate that reduces particle bounce. The sampling inlet uses a 50% cut-point for 2.5 and for 10 μm particles. For both impactors the smaller particles flow by the substrate and are

collected on a 47 mm filter and the remainder of the aerosol is exhausted (Figure 3-3). Changing the sampling medium involves removing the filter cassette and replacing it with another cassette containing a filter and impaction disk. The high flow rate provides increased sensitivity to low levels of PM (SKC, 2006).

Gravimetric sampling requires particle size separation through impaction and several steps are required for successful analysis. In systems where a plastic cassette is used to hold the filter, equilibration for at least 24 hours in a balance room in which temperature and humidity are controlled prior to weighing is necessary. Omitting this step may introduce a high degree of error to the overall data. A cassette can have its mass reduced by 1.5 mg in 4-5 days when exposed to drying conditions and can experience a similar increase in weight when left out in a humid environment (Smith, *et.al*., 1998). Weight measurements must use the appropriate analytical balance with sensitivity appropriate to the amount of particulate being measured. However, because of the variability in filters and substrates the readability cannot be regarded as the "limits of detection" or in other words, the lowest quantity of a substance that can be distinguished from the absence of that substance within a stated confidence limit (Vincent, 2007).

Gravimetric analysis in this study consisted of desiccating and conditioning 47mm Whatman quartz QM-A filters (Whatman International Ltd, Maidstone, England) for a minimum of 24 hours in a climate controlled chamber, (70^{o} F ± 5^{o} and a 32% relative humidity ± 5%) in accordance with EPA Compendium Method 10-3.1, *Selection, Preparation and Extraction of Filter Material* (EPA,

Compendium Method, 1999), prior to being weighed on a Mettler MT5 microbalance (Mettler-Toledo, Inc., Columbus, OH). Tare weight was measured twice and averaged prior to field sampling. After sampling, the cassette was equilibrated for 24 hours in the same balance room, and was weighed twice. The gross weight was subtracted from the tare weight resulting in the net weight or captured mass. The captured mass was divided by the unit volume of air sampled and the results expressed the measured concentration in mg/m^3. The weight and reference sample number were recorded on a control sheet (RTI, 2003).



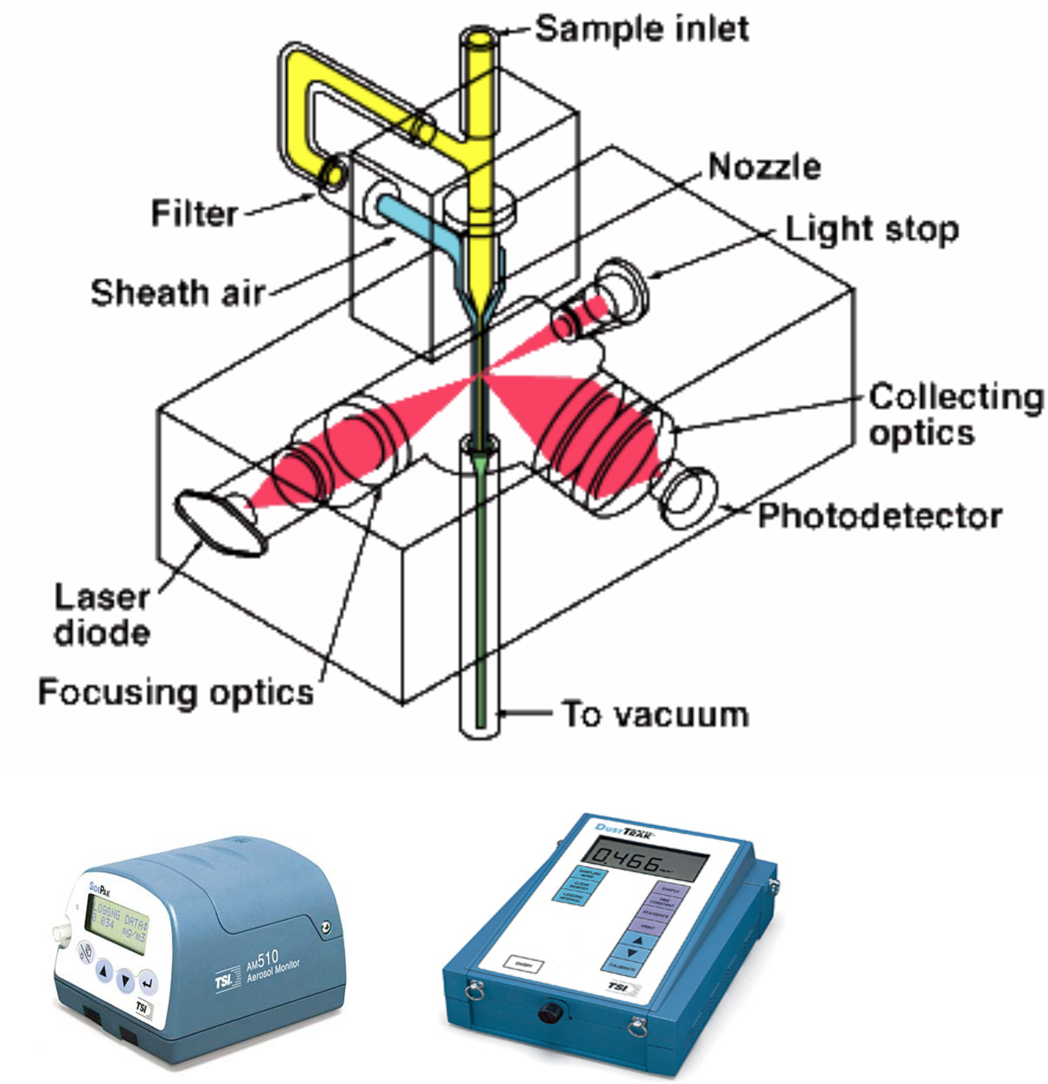
Exploded view of IMPACT Sampler

SKC® DPS, 2006

Figure 3-3. Exploded view of the SKC IMPACT sampler and an image of the SKC Leland Legacy aerosol pump with impactor inlet. The aerosol is drawn into the desired cut-point impactor inlet and larger particles are captured on the oiled impaction disk. The particles being sampled are then deposited on the collection filter. The installation of the rain cover does not affect the collecting efficiency of the sampler.

Photometric instruments employ light scattering technology to determine mass concentration in real-time. Both photometric instruments studied here can be fitted with inlet conditioners (impactors) that permit 1.0, 2.5, or 10 μm cut-points. After passing the impactor inlet, an aerosol sample is inspired into the sensing chamber in a continuous stream. A laser illuminates a section of the aerosol stream and particles in the aerosol stream scatter light in all directions. A lens situated 90° to the aerosol stream and the laser beam collects some of the scattered light and focuses it onto a photodetector. The detection circuitry converts the light into electrical current, which is proportional to the amount of light scattered and with calibration is assumed proportional to the mass concentration of the aerosol (Figure 3-4). The internal calibration constant is determined from the ratio of the voltage response to the known mass concentration of a test aerosol (TSI, 2002).

The sampler pump is factory calibrated, however good sampling technique would dictate that the instrument is tested and calibrated prior to sampling. A photometric instrument sampling an aerosol from the environment is likely to respond differently compared to the test aerosol used to calibrate the photometer. The accuracy of the instrument depends on the measured test aerosols having nearly the same aerosol concentration that would be needed to scatter light identically for the environmental sample. If there is a large difference, a systematic error may be introduced which can be controlled for by calibrating the instrument to the type of airborne particulate matter being sampled (Chen and Pui, 2008).



SidePak AM510 DustTrak 8520 TSI, 2006

Figure 3-4. The internal schematic of the photometric sampler and pictures of the TSI SidePak AM510 personal aerosol monitor and the DustTrak 8520 aerosol monitor. The aerosol is drawn into the sample inlet and particles travel down the inlet where they are detected by the laser and the photodetector. A portion of the air passes through a filter and then envelopes the particle stream; this air is known as sheath air. Sheath air surrounds the particle stream as it passes through the sensors in order to keep the optics clean.

The DPS is self-contained in an environmental enclosure and deployable at any location where the sampler head can be affixed at breathing zone height (approximately 180 cm). The DustTrak requires two cases, one for the instrument and its related paraphernalia and the second is the environmental enclosure. Deployment of the DustTrak required a sturdy raised platform at breathing zone height as the sampler inlet is fixed to the environmental enclosure. The SidePak is a personal aerosol monitor designed to be worn by an individual, however it was deployed alongside the other instruments with no difficulties.

Pump flow rate and calibration are critically important when sampling. The DPS pump was set for a flow rate of 10.0 LPM and the DustTrak and SidePak flow rates were adjusted to 1.70. LPM. These volumetric airflow rates were measured and adjusted before each sampling period, and were measured after sampling to assure the flow rate was maintained. At this flow rate, the DPS inspired 14.4 m^3/ day and the DustTrak and SidePak inspired 2.4 m^3/day. The BIOS DryCal® DC-Lite was used to calibrate the pumps. The DryCal, model number DCLT Rev. 1.08, was used to calibrate the DPS instruments as they have a high flow rate and the DryCal DCL ML Rev. 1.08 was used to calibrate the photometric instruments, which have a lower volumetric flow rate.

Statistical analyses used SigmaPlot® and MedCalc® software. The mean mass concentrations for the DPS, the DustTrak, and the Sidepak, were calculated for all measurements taken. The statistical analyses: the PMCC, the correlation within means, and the Bland-Altman analysis were used to determine

the relationship of data between the instruments. The correlation coefficient analyses indicate the strength and direction of a linear relationship. The PMCC determined if a correlation existed between the instruments when compared temporally and spatially. The correlation within means used the data averaged from all the instruments each day, and the purpose of the correlation within means analysis was remove the factor of location in the event that there were any site specific anomalies. Systematic bias could exist from external influences, and would affect the accuracy of the statistical measurement. The third analysis, the Bland-Altman analysis, was used to compare the two different measurement techniques and determine by how much one method of assessing airborne PM concentrations differed from the other.

The Bland-Altman analysis is a statistical method that allows the investigator to compare two different measurement techniques to determine the degree of agreement between variables as opposed to the strength of a relationship (Bland-Altman, 1986). The analysis investigates any possible relationship between measurement error and the estimated true value. As the true value is unknown, the mean of the two measurements being compared serves as the estimated true value.

The Bland-Altman analysis compares measurement techniques against a reference value. This is particularly useful when the reference value may not have an accepted standard. Bland and Altman suggest when a technology has bias and precision comparable with the accepted technology; it may be used as an alternative. In essence, the analysis is used to know by how much one

method is likely to differ from the “acceptable” method and if it is not enough to cause problems then the two can be used interchangeably (Bland-Altman, 1986). The limits of agreement are only estimates of the values that apply to all of the data points in the sample analyzed and the statistics are only valid for that comparison (Bland-Altman, 1995).

Results and Discussion

The results are presented in Table 3-1 and Table 3-2. The analysis between the DPS and SidePak was discarded, as the power source did not enable the SidePak to sample for a twenty-four hour period. Battery life in the SidePak instruments averaged 8.6 hours when using the rechargeable nickel-metal hydride (NiMH) batteries (P/N 801728) and 16.7 hours with Energizer® AA E91 alkaline batteries. The battery life was considerably less than that claimed by TSI, which stated, 15.6 hours with the NiMH batteries and 22.5 hours with the Energizer® AA E91 alkaline batteries (TSI, 2006). The NiMH batteries were charged and tested at 100% full battery capacity prior to installation and the alkaline batteries were tested to be at 100% capacity. All of the instruments were effective in collecting airborne PM by maintaining a constant flow rate; start and end flowrates were measured to be within ± 5%, operating over the entire 24-hour sampling period.

The maintenance of the DPS, the DustTrak, and the SidePak was minimal and easily accomplished in the field. A 284g can of pressurized gas, difluoroethane (CAS: 75-37-6), as used for cleaning computer parts facilitated cleaning and ensured the cleanliness and operability of the samplers used.

The DustTrak and SidePak were nonprogrammable using currently available computers. The samplers use an obsolete computer interface, a nine pin serial cable, which is not commonly found on up to date computers. Two different nine pin to USB connections were tried and connectivity was found to be intermittent and unreliable. The instruments were therefore manually programmed which limited their capabilities by not being able to enter sampling start, end, and sampling frequency times. Downloading data from both instruments using the USB connection mentioned above resulted in multiple error messages. Subsequently, it was discovered that TSI declared the DustTrak 8520 obsolete in October of 2008; it is unlikely that any upgrades will be made to this model.

To provide sufficient latitude in interpreting the data a determination of how correlations were to be assessed was established. Too small or large a cut-off point between categories would be unsatisfactory considering that no other studies were located upon which to make a comparison. Correlation in this study is similar to that used by Simon (2008):

- -1.0 to -0.7 strong negative association
- -0.7 to -0.3 weak negative association
- -0.3 to +0.3 little or no association
- +0.3 to +0.7 weak positive association
- +0.7 to +1.0 strong positive association

The PMCC significance level was set at 0.05 for the overall correlation temporally and spatially for individual comparisons between the gravimetric and respective photometric instruments as individual units operated together at

discrete locations. Data from the DPS and DustTrak were strongly correlated for PM_{10} (r= 0.806, Table 3-1).

The correlation within means was used to analyze the data averaged from the gravimetric instruments to data averaged from the DustTrak instruments for each day. The analysis compared the measured mass concentrations of airborne $PM_{2.5}$ and PM_{10} data from all DPS instruments against all DustTrak instruments, which resulted in a stronger correlation of data compared to the PMCC results (Table 3-1, Figure 3-5). The correlation within means data for PM_{10} comparing the DPS and DustTrak provided a value for r of 0.949. The data correlation between the DPS and the DustTrak instruments sampling for $PM_{2.5}$ had a weak PMCC correlation of 0.241 and 0.041 for the correlation within means analysis (Table 3-1).

	Pearson correlation (R)	Correlation within means (R)	Significance
DPS - DustTrak PM10	[1] 0.806	0.9491	[1] $p = 0.01$
DPS - DustTrak PM 2.5	[2] 0.241	0.4110	[2] $p= 0.386$

Table 3-1. Data for the Pearson correlation coefficient and correlation within means. The data show a strong correlation when sampling for airborne PM_{10} and a weak correlation when sampling for $PM_{2.5}$.

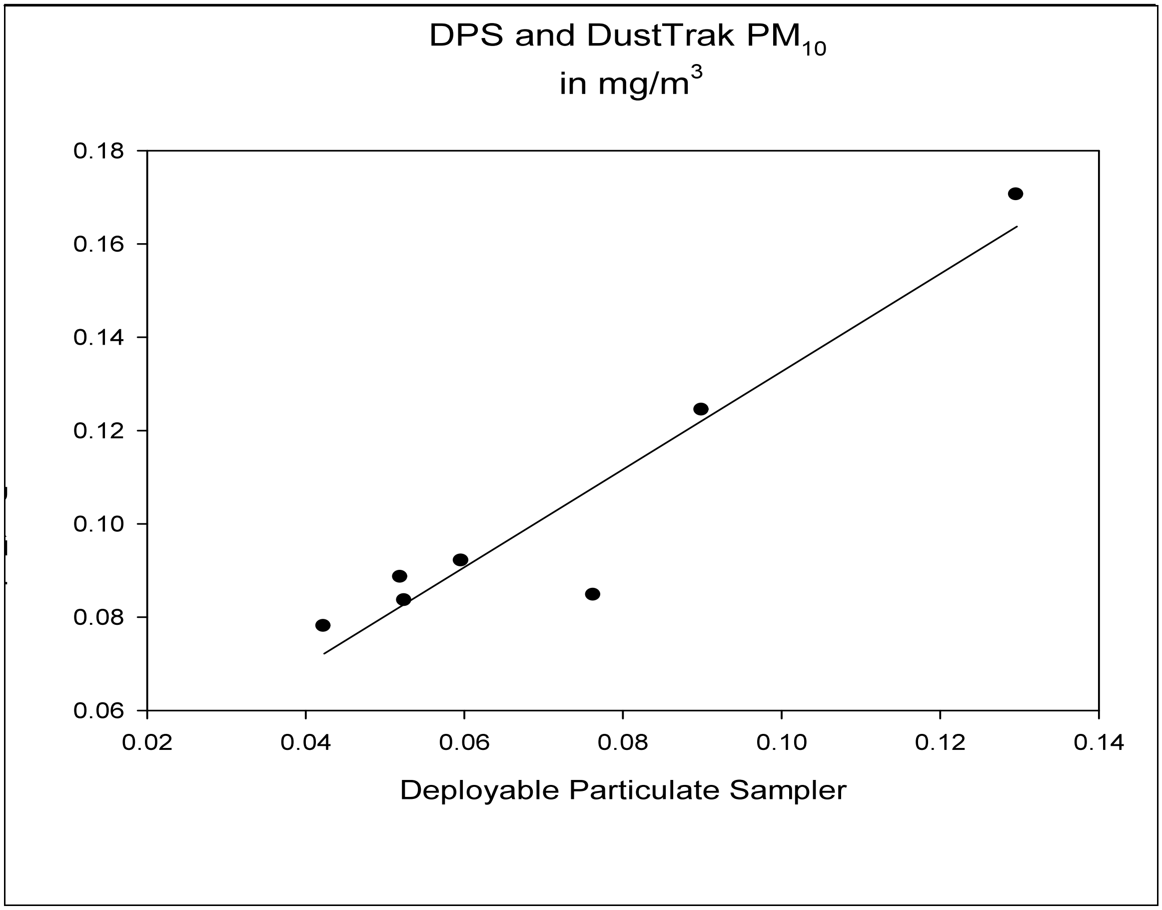


Figure 3-5. Data plot for the correlation within means between the DPS and DustTrak when sampling for airborne PM_{10}.

The Bland-Altman difference against means for the analyses resulted in most of the variables falling within the 95% limits of agreement, thus 95% of the differences were within ± 2 standard deviations. The resulting plot allows the investigator to determine bias, which is the average difference, and the ideal bias, which equals zero. The limits of agreement are illustrated (Figure 3-6) to two standard deviations that describes the range for 95% of the comparison points based on an assumption of normal differences. The data in Table 3-2 and the graph in Figure 3-6 have very small limits of agreement and a small variation of the differences; the mean is very close to the ideal bias of zero. This analysis would suggest that the DPS and the DustTrak could be used to quantify airborne PM for the conditions that existed during testing. The results that were obtained in the study suggest that there is not enough of a difference between the measurement methods to cause problems and the limits of agreement are small enough to be confident a relationship exists between the instruments and the data.

Paired Data	Average Difference	Lower 95% Limit of Agreement	Upper 95% Limit of Agreement
DPS - DustTrak PM10	-0.03	-0.09	0.03
DPS - DustTrak PM 2.5	-0.0028	-0.0338	0.0282

Table 3-2. Bland-Altman Difference against Means mass concentration in mg/m^3. The average difference between the data are very small and the upper and lower limits of agreement are narrow.

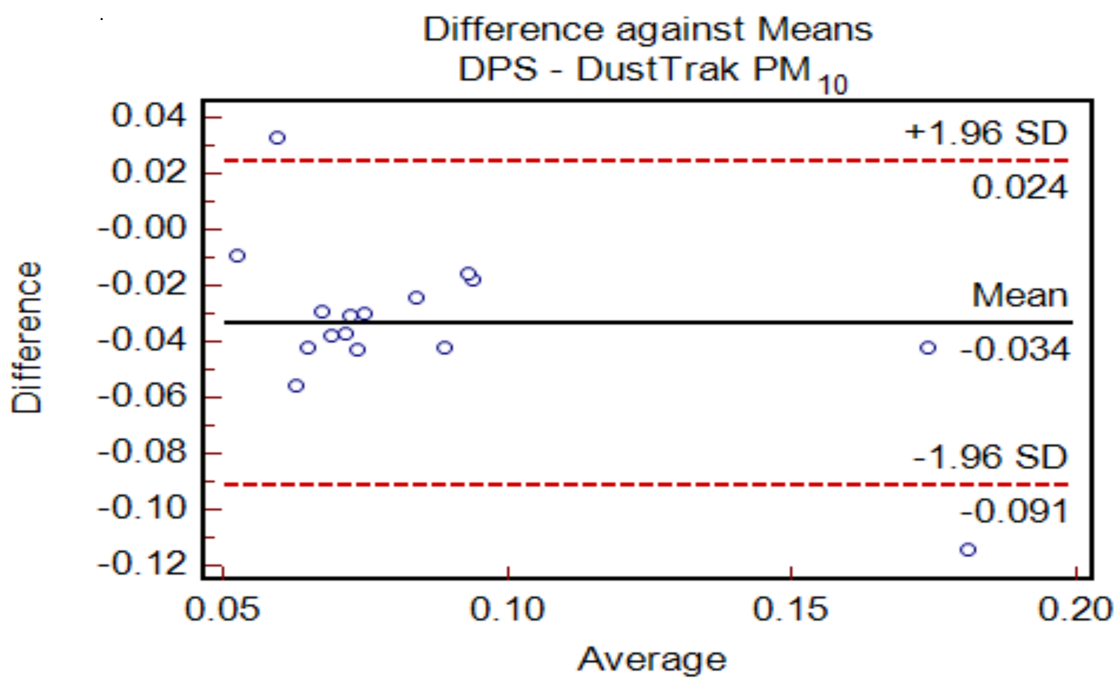


Figure 3-6. The Difference against Means between the DPS and DustTrak when sampling for PM_{10}. The mean of the data is very close to zero, which suggests very limited bias. As well, the upper and lower 95% limits of agreement are very narrow and most of the data points fall within these limits.

An overall analysis demonstrated a strong correlation of data between the DPS and DustTrak when sampling for airborne PM_{10} but a weak correlation of data when sampling for airborne $PM_{2.5}$. While correlation shows the comparison between two different measurements, it may not have been suitable to use when comparing aerosol measurements from gravimetric and photometric instruments. The photometric measurements have numerous associated variables that can cause error such as, low airflow or software problems. The Bland-Altman method results indicate a good relationship between the DPS and DustTrak instruments when sampling for $PM_{2.5}$ and PM_{10} based on measurement error and the estimated true value. The combined results would suggest a quantitative relationship between the DPS and DustTrak when sampling for $PM_{2.5}$ and $PM_{10,}$ however, because of the disparities in the analyses it is not enough of a relationship to determine that the instruments are interchangeable in all situations.

Gravimetric and photodetection instruments have their limitations and applications that necessitate consideration when devising a sampling plan. However, when taken into consideration they can complement one another when conducting aerosol sampling. For example, if a large increase in photometric instrument response is used to assess a potential leak in a process where aerosol is generated, the gravimetric instrument may be used to follow-up and provide a quantitative sample for further analysis.

One DPS system out of three became unusable after nine days of operation from a pump malfunction that limited useable data for the PMCC analysis. One

TSI SidePak instrument out of three became unusable due to unreadable display characters. The computer interface problems and lack of validated USEPA reference methods were disadvantages for use of the photometric instruments.

Additional research in this area would greatly enhance the users understanding of the instruments' capabilities and limitations. Laboratory research with known standards of various particle size distributions and photometric properties, would assure the operator the results they are obtaining are reliable. A better understanding of the systems would improve data collection methodology and enhance exposure data collection.

Conclusion

The hypothesis of this research is that comparable environmental sampling results are obtained using either the gravimetric SKC® Deployable Particulate Sampler or the photometric instruments: the TSI® DustTrak™ 8520 and Sidepak™AM510 aerosol monitors, at the 2.5 and 10 µm aerodynamic diameter cut-points. The data suggest that a relationship exists between the DPS and the DustTrak sampling for PM_{10} however, sampling data for $PM_{2.5}$ demonstrated a weak correlation but an acceptable degree of agreement using the Bland-Altman analysis. The disparity in the analytical results from both $PM_{2.5}$ and PM_{10} data obtained during this study does not fully support the hypothesis that the instruments can be used interchangeably.

Conducting tests with aerosol of known geometry and varied photometric properties in a controlled laboratory environment would provide information regarding the range limits, accuracy, precision, repeatability, and identification of

possible conditions that would detrimentally influence the quality of samples taken by the instruments and would help to resolve the issue of instrument interchangeability.

The specific aims of this research were met. The collection of airborne $PM_{2.5}$ and PM_{10} in a desert environment were completed and the results statistically analyzed to determine that a relationship between data exists for the DPS and the DustTrak instrument at the PM_{10} cut-point; however, the comparison at the $PM_{2.5}$ cut-point was weak. The data analyses for the DPS and SidePak was negated because the SidePak was unable to sample for a 24-hour period. All of the instruments were effective in collecting airborne PM by maintaining a constant flow rate; start and end flowrates ± 5%, operating over the entire 24-hour sampling period, except for the Sidepak, collecting, or monitoring airborne PM, and were suitable for use in this environment. The performance of the instruments with regard to effectiveness, as defined by producing the desired results, was the instruments were good at collecting data, however the computer interface problems with the TSI instruments and the fact that one DPS and one SidePak instrument failed beyond user reparability was a detriment to the study.

Further research in this area, both in the laboratory and in the field may reveal beneficial results that could increase the abilities of health protection services to protect military forces by measuring potentially harmful airborne PM and thus, minimizing exposure to potentially hazardous environmental conditions.

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